Characterisation of oil and aluminium complex on replica and historical 19th c. Turkey red textiles by non-destructive diffuse reflectance FTIR spectroscopy

Julie H. Wertz[a], Pik Leung Tang[b], Anita Quye[a*] and David J. France[c]

[a]Centre for Textile Conservation, University of Glasgow, 56 Dumbarton Road, G11 6AQ, UK.

[b]Agilent Technologies, 5 Lochside Avenue, Edinburgh Park, Edinburgh EH12 9DJ, UK.

[c]School of Chemistry, University of Glasgow, University Avenue, G12 8QQ, UK.

Abstract

This work investigates historical and replica Turkey red textiles with diffuse reflectance infrared (DRIFT) spectroscopy to study the coordination complex between cellulose, fatty acids, and the aluminium ions that form the basis of the colour lake. Turkey red was produced in Scotland for around 150 years, and is held in many museum and archive collections. The textile was renowned for its brilliant red hue, and for its fastness to light, washing, rubbing, and bleaching. This was attributed to its unusual preparatory process, the chemistry of which was never fully understood, that involved imbuing cotton with a solution of aqueous fatty acids and then aluminium in the following step. Here we show, for the first time, a characterisation of the Turkey red complex on replica and historical textiles. The development of techniques for non-destructive and *in situ* analysis of historical textiles is valuable for improving understanding of their chemistry, hopefully contributing to better conservation and display practices. The results show the fatty acids condense onto the cellulose polymer via hydrogen bonding between the C=O and OH of the respective compounds, then the aluminium forms a bridging complex with the fatty acid carboxyl. This contributes to an improved understanding of Turkey red textiles, and shows the useful application of handheld diffuse FTIR instruments for heritage textile research.

Keywords: Diffuse reflectance spectroscopy, Turkey red, textiles, in situ analysis, heritage conservation science, metal carboxylates

1 Introduction

The brilliant dyed textile known as Turkey red (see Figure 1a and 1b), also called Adrianople red, *rouge d'Andrinople*, *rouge turc*, and *Türkischrot,* was created through a complicated and unusual eponymous dyeing technique. Eminent pioneering chemists such as Berthollet [1] and Chaptal [2] attempted to elucidate the chemistry of Turkey red, which was considered key to understanding its legendary fastness to light exposure and washing. It was produced in the west of Scotland for around 150 years, from 1785 to 1936, when improved synthetic red dyes were finally of a quality to compete with Turkey red [3]. Despite extensive research and experimentation on the process and textile, the chemistry of Turkey red remained elusive throughout the 20th c. Although no longer in production, examples of historical Turkey red can be found in many museum and archive collections [4].

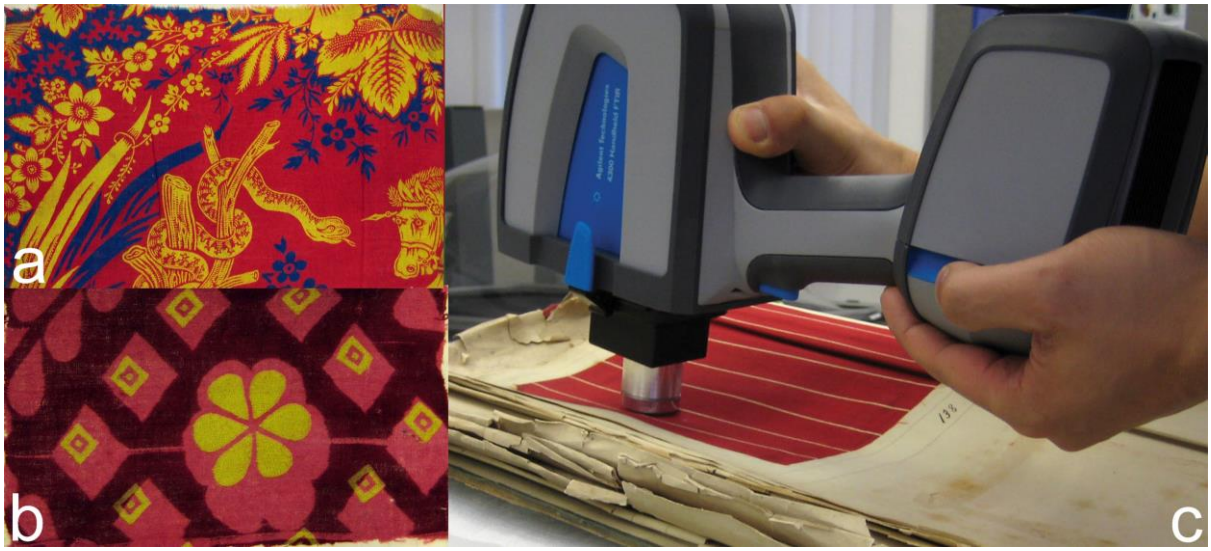


Figure 1a: UGD 13/8/6 #11. Figure 1b: UGD 13/8/7 #11. University of Glasgow Archive Services, Records of United Turkey Red Co. Ltd, GB 248. Figure 1c: Handheld FTIR analysis of historical Turkey red from the Glasgow University collection.

This research aims to finally understand the unique chemistry of Turkey red by characterising the complex responsible for the colour, forming a basis for improved conservation and display practices for these objects through a non-invasive conservation-based analytical technique. The analysis can also be used to screen textiles in collections, a valuable tool for curators and conservators. Turkey red exists only on dyed cellulose fibres, and cannot be found as a powder or liquid [5]. To study the bonding of the complex, analysis must be done *in situ* on the fibres. It is suspected that the treatments do not affect the cellulose polymer structure, based on the condition of historical Turkey red showing no signs of degradation, and the mild conditions of the dyeing

process. The hypothesis is that a surface coating forms between cellulose hydroxyls and fatty acid carbonyls/carboxyls. The analysis of heritage materials requires careful selection of techniques to both answer the question at hand and minimise the impact on the object, with an emphasis on non-invasive and *in situ* analysis whenever possible. Infrared spectroscopy (IR) is a useful analytical tool for studying molecular bonds and bonding interactions in organic materials such as surface coatings. Fourier transform IR (FTIR) in reflectance modes offers such possibilities and has proved particularly useful in conservation science research [6]. In 1965, research by Kiel and Heertjes on complexes of metals and alizarin (see Figure 2) using IR (prior to the development of Fourier transform technology) included an investigation of historical Turkey red and identified spectral bands corresponding to the uptake of fatty acids, though they did not explore the nature of the bonding to the cellulose [7,8]. Their analysis was carried out by removing samples from 19th c. dyeing manuals and preparing potassium bromide pellets from the textiles. The recent development of handheld diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy instruments (Figure 1c) has been advantageous to heritage conservation science [9–11]. The diffuse reflectance interface is also better at detecting scattered light from uneven textile surfaces [12], yielding more detailed spectra. This work improves upon the study by Kiel and Heertjes by examining whole fibres, *in situ*, using a Fourier transform instrument, and characterising the oil-cellulose bond.

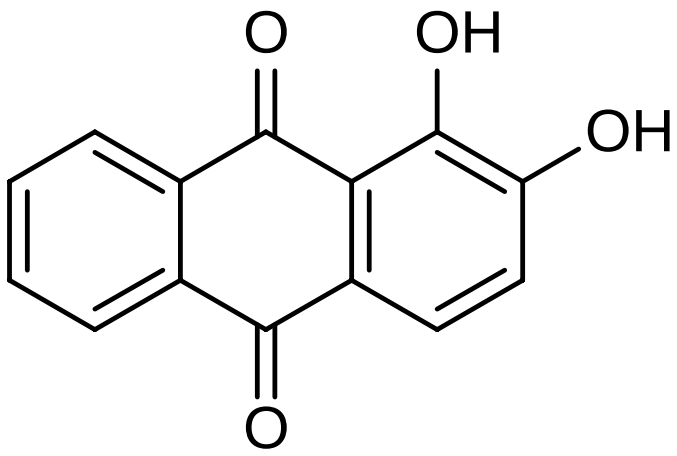


Figure 2 Structure of alizarin, a hydroxyanthraquinone dye and the most abundant component of madder.

DRIFT spectroscopy is applied here to historical 19th c. Turkey red textiles from United Turkey Red (UTR) (Figure 1a and 1b) and historical samples exemplifying the preparatory stages of oiling the calico for Turkey red colouration in a textile dyeing manual of the type studied by Kiel and Heertjes. It required no sampling or alteration of the historical textiles, and the samples on the pages could be analysed *in situ*. Prior to the analysis of the historical samples, replicas of oiled calico and of Turkey

red-dyed calico were prepared following a historical process from Hummel [13] to develop the DRIFT methodology for detection and identification of signature compositions for historical Turkey red calico.

Infrared radiation is absorbed, reflected, scattered, and refracted based on the instrument interface; in DRIFT the detector collects diffuse reflected light and surface-reflected, or specular reflected, light. This causes distortion of the spectra in the form of derivative-like features and inverted, or restsrahlen bands, which can be corrected with a Kramers-Kronig or Kubelka-Munk algorithm. In the handheld devices, the ratio of specular and diffuse light collected depends on surface roughness of the sample. The applicability of the transformations varies based on the specular component, and can be affected by the morphology and composition of the object. If an algorithm is not used, the intensity is described as pseudo-absorbance A' or log(1/R)[10,14,15]. The raw spectra in this analysis did not show any inverted bands and are presented as log(1/R).

2 Turkey red dyeing

A true Turkey red process requires cellulose fibres, almost always as cotton, which must be treated with an oil bath. The initial oil treatment is imperative to dyeing Turkey red and distinctive to the technique, making it an interesting and useful chemical marker. From the mid-18th c. when production in Europe began, Turkey red dyers usually prepared their cotton using rancid olive oil, also called *huile tournante*, mixed with weak aqueous sodium carbonate. This became known as the 'old' process around the early 1870s with the development and adoption of sulfated castor oil, which was known as Turkey red oil, and was made by treating castor oil with sulfuric acid and neutralising it. In this 'new' process, the water-soluble Turkey red oil could be more efficiently applied and the excess removed prior to applying aluminium in the next step. The higher fatty acid content of the Turkey red oil relative to the naturally rancid olive oil reduced the number of necessary oil treatments, cutting the overall time to dye Turkey red down from around three weeks to three days [16]. The 'old' and 'new' oiling techniques both had the aim of imbuing the cotton fibres with fatty acids, which are necessary to form the foundation of the Turkey red complex. Turkey red is 'built' on the fibre by the further addition of aluminium, either aqueous aluminium acetate or aluminium potassium sulfate. Dyeing is done in an aqueous bath containing calcium, usually calcium carbonate, and anthraquinone dye. These form a lake, an insoluble complex of organic colorant molecules and metal ions, with the aluminium. The main colourant was alizarin, which came from either ground madder root (primarily *Rubia tinctorum* L., dyer's madder) or as synthetic manufactured from anthracene after the mid-19th c. [17] The final step is called clearing or

brightening, and was done by boiling the dyed cotton in water with shaved olive oil soap and sodium carbonate, or occasionally with wheat bran.

3 Experimental

3.1 Preparation of replicas

3.1.1 Replica oiled calico samples

Medium-weight calico (Whaleys Bradford) was scoured twice by simmering it in a stainless-steel kettle in 5 g/L aq. Na_2CO_3 (soda crystals, DriPak) for an hour, then rinsing it in running water and air drying them. Twelve samples approximately 3 cm by 5 cm each were cut and divided into two groups. The six control samples were saturated with ultrapure water (Millipore Direct Q 3 UV, 18.2 MΩ resistivity). A solution of aq. Turkey red oil was prepared with 2.05 g Turkey red oil sodium salt (microscopy grade, Fluka) and 2.06 g ultrapure water. The oil was applied to the other six samples with a dropper until the fibres were saturated, then the excess oil was wrung gently under finger pressure. Five samples from each set were placed in separate glass dishes, and both sets were placed in an oven (Heraeus Function Line 110 L) at 60 °C ± 3 °C. Two reserved samples were kept at room temperature (avg. 20 °C and 79% RH) for 30 days. One oiled sample and one control were removed from the oven after 24 h (1 day), 240 h (10 days), and 504 h (21 days), and two sets were removed at 96 h (4 days). The time points selected here are longer than the ca. 24 hours specified in the literature on Turkey red dyeing, but these samples were designed to observe the effect of heat exposure over time on oil adsorption by the cotton. One of the 4-day oiled calico preparation sets was subjected to an additional steaming treatment, a technique that appears in some late-19th c. Turkey red oiling processes. The steam treatment was done by placing the samples on the metal rack of a commercial pressure cooker (Fagor Elite 4 qt) with 300 mL of water, closing the system and heating it to the operating pressure of approx. 15 psi (according to manufacturer) for 90 minutes. After depressurisation of the system, all samples were rinsed individually in flowing tap water and left to dry at room temperature (see Table 1).

Treatment	Exposure (days)	Sample
Water	1	W1
	4	W4

	4 + steaming	W4s
	10	W10
	21	W21
	30 (no heat)	WA
Turkey red oil	1	TRO1
	4	TRO4
	4 + steaming	TRO4s
	10	TRO10
	21	TRO21
	30 (no heat)	TROA

Table 1 Samples of replica oiled calico.

3.1.2 Replica Turkey red samples dyed by the new process

Replica Turkey red was dyed with madder and with synthetic alizarin (Figure 3). Squares of medium-weight calico about 4.5 cm x 4.5 cm were cut from the scoured calico described in the previous section. A solution of 25 g Turkey red oil and 50 g ultrapure water was mixed and applied dropwise to the samples as before, then they were placed in the oven at 60 °C for 24 hours. The samples were placed in a ceramic dish with a loose aluminium foil cover to allow air circulation and protect the samples from condensation. The dish was placed in a commercial pressure cooker and the system heated to operating pressure for 60 minutes. After the cooker was depressurised, the samples were removed and rinsed well in flowing water, then left to air dry.

An alum solution was prepared by dissolving around 100 g of $KAl(SO_4)_2 \bullet 12H_2O$ (reagent grade, Sigma-Aldrich) in 100 mL of ultrapure water heated to 70 °C, then allowing it to cool. A saturated aq. solution of sodium carbonate (≥99.5%, Fisher) was added a few drops at a time, while stirring, until the colourless flocculation precipitated by the alkali no longer dissolved back into solution. About 1 mL of Na_2CO_3 solution was used before the clear, colourless solution became slightly opalescent, when addition was stopped. Ultrapure water was added until the solution tested at 8 °Tw with a hydrometer (0-24 °Tw, Brannan) as directed by Hummel's method [13]. The °Tw, or Twaddell scale, used in Hummel and other texts, measures specific gravity of liquids denser than water (0 °Tw) up to 2 g/mL (200 °Tw), with 8 °Tw approximately 1.04 g/mL. The bath was heated to 50 °C and the dried, previously oiled calico samples submerged and stirred regularly with a glass rod. The samples were

left for four hours, during which the solution became opaquer as a colourless precipitate formed. Afterward, the samples were removed from the bath and wrung under finger pressure, then placed in the oven at 75 °C until dried. They were rinsed well in flowing water and left to air dry.

The samples were dyed in two groups of three, each weighing about 2 g in total. The synthetic alizarin bath was prepared by weighing about 40 mg of alizarin (97% purity, Acros Organics) and 15 mg $CaCO_3$ (99% purity, Alfa Aesar) into about 800 mL of ultrapure water in a 1 L glass beaker. The madder bath was prepared by soaking 6 g ground *R. tinctorum* (Couleur Garance) overnight in 30 mL of ultrapure water, then draining the liquor to remove water-soluble impurities [18]. The wet madder was added to 800 mL ultrapure water in a separate 1 L glass beaker with around 15 mg $CaCO_3$. Both beakers were covered with watch glasses to reduce evaporation and stirred regularly with glass rods. The samples were left in the cold dye baths for 30 minutes, then the temperature raised to 70 °C over a period of 90 minutes and held for a further 60 minutes. At this point, both madder and alizarin samples had become a deep, vivid red. The samples were removed from the dye bath and rinsed well in flowing water until the runoff was colourless.

The final step in Turkey red dyeing is called 'clearing' in the historical texts. The samples were kept separate according to whether they were dyed with madder or synthetic alizarin. For each group, a clearing bath was prepared in a 2 L lidded aluminium kettle with 500 mL water and 2 g each Na_2CO_3 (DriPak) and flaked Marseille olive oil soap (L'Occitane en Provence). The samples were submerged and the temperature raised to a gentle boil with the lid loosely covering the kettle to reduce evaporation and vent steam, with water replaced as needed to maintain the original volume. Afterward, the bath was a deep red shade. The samples were again rinsed well in flowing water and left to dry at room temperature (see Table 2).

3.1.3 Madder-dyed calico

A sample of calico was dyed with aluminium and madder but without an oil treatment following a recipe from Fereday [18]. A piece of scoured calico weighing 1.5 g was heated in a bath of 500 mL ultrapure water with 0.2 g tannic acid (reagent grade, Sigma-Aldrich) to 80 °C over 1 hour, then lowered to 60 °C and held for 1 hour. The calico was left overnight to cool in the tannin solution, which was then heated to 80 °C over 1 hour before removing the calico and rinsing it in flowing tap water. The tannin-treated calico was then added to bath of 0.8 g $KAl(SO_4)_2 \bullet 12H_2O$ (alum) in 500 mL water and heated to 60 °C over 1 hour, held at this temperature for 90 minutes, then the calico left overnight in the alum solution to cool. The next day the alum bath and calico were re-heated to 60

°C over 1 hour and left to cool again. The dye was prepared by soaking 3.2 g ground madder overnight in 10 mL ultrapure water, then the liquid pour off and the madder added to 500 mL ultrapure water. The calico was removed from the alum bath, rinsed in flowing water, and added to the madder bath. The temperature of the dye bath with the calico was raised to 80 °C over 1 hour, then boiled for 2 hours, left overnight to cool, re-heated the next day to 65 °C over 1 hour and left to cool again. The dyed calico was finally rinsed in flowing water tap and left to dry at room temperature.

Dye	Replicate	Sample
Turkey red, madder	1	TRM1
	2	TRM2
	3	TRM3
	gift	TR*
Turkey red, alizarin	1	TRA1
	2	TRA2
	3	TRA3
Madder (no oil)	1	M
	gift	M*

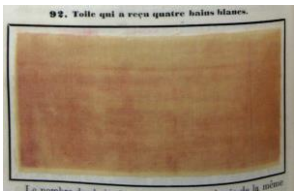
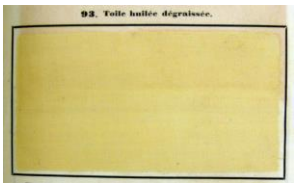
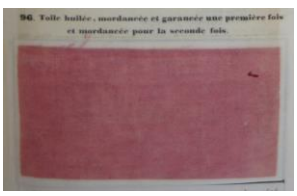
Table 2 Samples of replica Turkey red and calico dyed with madder.

Figure 3 Replica Turkey red and calico dyed with madder.

3.2 Historical Turkey red samples

DRIFT spectra were taken from historical oiled calico and Turkey red samples in *Traité théorique et pratique de l'impression des tissus, vol. 3* by Jean-François Persoz, published in 1846 [19] (Table 3) and found in the Glasgow University Special Collections (Sp Coll RB 5054).

Spectra were also taken from commercially-produced Turkey red textiles dating from 1886-1887, in the UTR collection in the Glasgow University Scottish Business Archive (SBA) (Figure 1a and 1b); three samples from each book were analysed for this paper.

Persoz sample	**Description**	**Translation**	**Image**
#92	*Toile qui a reçu quatre bains blancs*	Fabric oiled four times (colour transfer from opposite dyed sample)	
#93	*Toile huilée et dégraissée*	Fabric oiled and degreased	
#95	*Toile huilée, mord, et teinte une 1er fois en garance*	Fabric oiled, mordanted, and dyed once with madder	
#96	*Toile huilée, mordancée et garancée une première fois et mordancée pour la seconde fois*	Fabric oiled, mordanted, and dyed with madder once and then mordanted a second time (shown with original protective paper)	

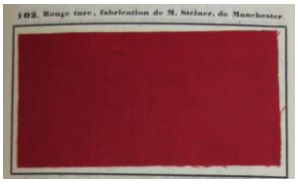
#97	*Toile huilée ayant reçu deux fois le mordant et qui a passé deux fois dans un bain de garance*	Fabric oiled and mordanted twice, then dyed twice in madder	
#98	*Toile huilée et garancée qui a reçu le premier avivage*	Fabric oiled and dyed with madder and cleared once	
#100	*Toile huilée et garancée qui a reçu le troisième avivage*	Fabric oiled and dyed with madder then cleared three times	
#101	*Toile huilée, garancée, avivée et passé en son*	Fabric oiled, dyed with madder, and cleared with bran	
#102	*Rouge turc, fabrication suisse*	Turkey red, Swiss made	
#103	*Rouge turc, fabrication de M. Steiner, de Manchester*	Turkey red, from Steiner of Manchester	
#111	*Fond rouge turc, impression blanc enlevage à la presse écossaise (tissu croisé)*	Turkey red ground discharge printed white with a roller (fabric folded)	

Table 3 Numbered samples from Persoz, their original description, and a translation. *Traité théorique et pratique de l'impression des tissus*. Glasgow University Special Collections (Sp Coll RB 5054).

3.3 DRIFT analysis

DRIFT analysis was performed with an Agilent 4300 Exoscan FTIR portable spectrometer with a diffuse reflectance interface (Agilent Technologies). Spectra were obtained in absorbance mode from 5000-650 cm^{-1} at 128 scans per sample and a resolution of 8 cm^{-1}. The background was taken every 10 minutes using the instrument cap. For the replica textiles described earlier, six DRIFT spectra were taken of each sample from different positions by laying the instrument on its side and holding the sample to the interface (beam spot ca. 2 mm diameter). For the historical pieces, the instrument was held above the textile in contact with the surface, but with no load placed upon the object. Three spectra were taken from different positions on the textile and averaged prior to interpretation using Panorama Pro software (LabCognition). The data was converted to spectral graphs using Spectragryph, with an adaptive baseline correction applied before normalising to the highest peak. The figures show three segments of the spectra, a) 3000-2800 cm^{-1}, b) 1800-1400 cm^{-1}, and c) 950-800 cm^{-1}, where the changes from the Turkey red treatments are visible. The replica dyed calico textiles showed no physical signs of degradation, damage, or structural failure prior to, or after, analysis.

4 Results and discussion

4.1 Oiled calico

The DRIFT spectrum for the plain calico blank (Figure 4, red line) was consistent with previous FTIR analyses of cotton fibres [17,18], and used here to identify peaks in the oiled calico and Turkey red samples resulting from treatments to the cellulose. This spectrum is included in each figure for comparison. The full peak assignments for cotton are not provided here because this work focuses on the surface analysis of cellulose (cotton) fibres treated with fatty acids. The presence of fatty acids on the calico could be detected by the carbonyl (C=O) of the fatty acid carboxyl moiety, a functional group that does not appear in the cellulose polymer. Although cotton naturally contains fats and waxes that have a carbonyl, the scouring process prior to dyeing eliminates these substances. The spectra for the water-treated control set exposed to heat in Figure 4 are consistent with that of the calico blank, indicating the heat and water have no detectable direct effect on the

cellulose structure. The DRIFT spectra from the replica and historical oiled calico and Turkey red show peaks consistent with fatty acid treatments applied from the Turkey red process.

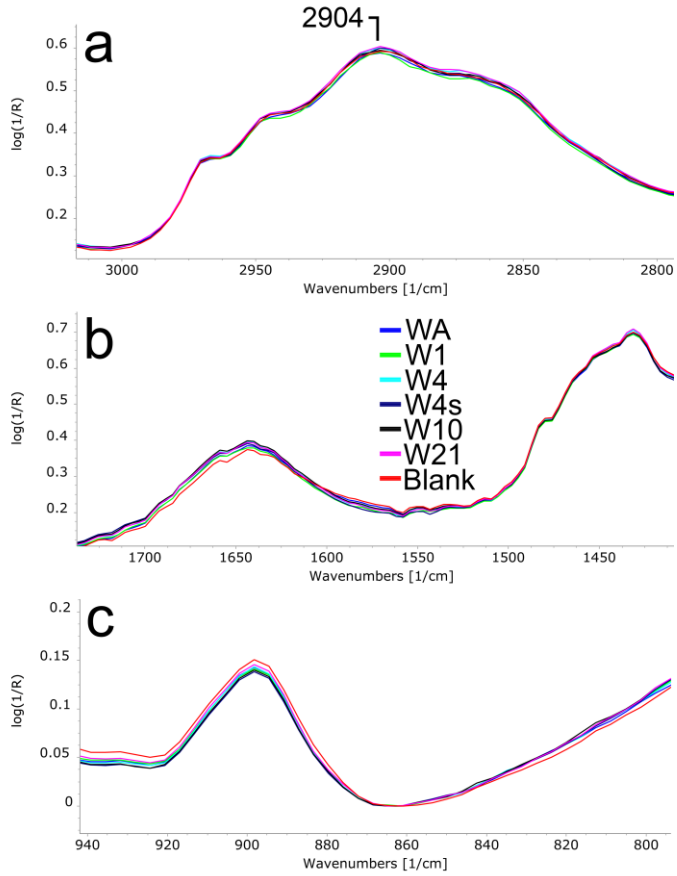


Figure 4 DRIFT spectra of calico control samples-treated with water and heated to 60 °C for increasing time points. Peak for W21.

To determine how the oil bonds to the cellulose to form the Turkey red complex, it was useful to compare these results to published FTIR studies of fatty acid coatings on hydroxyl-rich substrates. This approach was taken because the available research on fatty acid-cellulose bonding was done on modified forms of cellulose, e.g. microcrystalline or methylated, samples prepared in harsh, organic conditions [19,20], making it difficult to compare to the Turkey red process. Research on oleic acid coatings on apatite [24] (a group of phosphate minerals containing calcium and hydroxyl groups), and on oleic acid coatings on soda-lime-silicate glass [22,23], which are analogous to cellulose hydroxyls and prepared in aqueous conditions, were useful in this research to characterise the oil treatment. This bonding of fatty acids with surface hydroxyl groups in aqueous media in the presence of sodium, calcium, and aluminium ions is chemically similar to oiling cotton for Turkey red, but in the absence of the cellulose polymer. Turkey red oil contains ricinoleic acid, which is

structurally identical to oleic acid but with a hydroxyl at the C12 position, so the spectral results are comparable to those of samples prepared with oleic acid.

In Figure 5, the spectra for the oiled calico treated with aq. Turkey red oil solution show differences corresponding to the oil treatment that are not present in the control samples. In Figure 4, the stretch at 2904 cm^{-1} is marked for asymmetric $\nu_{str}(-CH_2-)$; in Figure 5a the two peaks are marked at 2911 and 2859 cm^{-1}, consistent with $\nu_{asym}(-CH_2-)$ and $\nu_{sym}(-CH_2-)$, respectively [27]. This is consistent with increased $-CH_2-$ on the samples from aliphatic chains in the oil treatment.

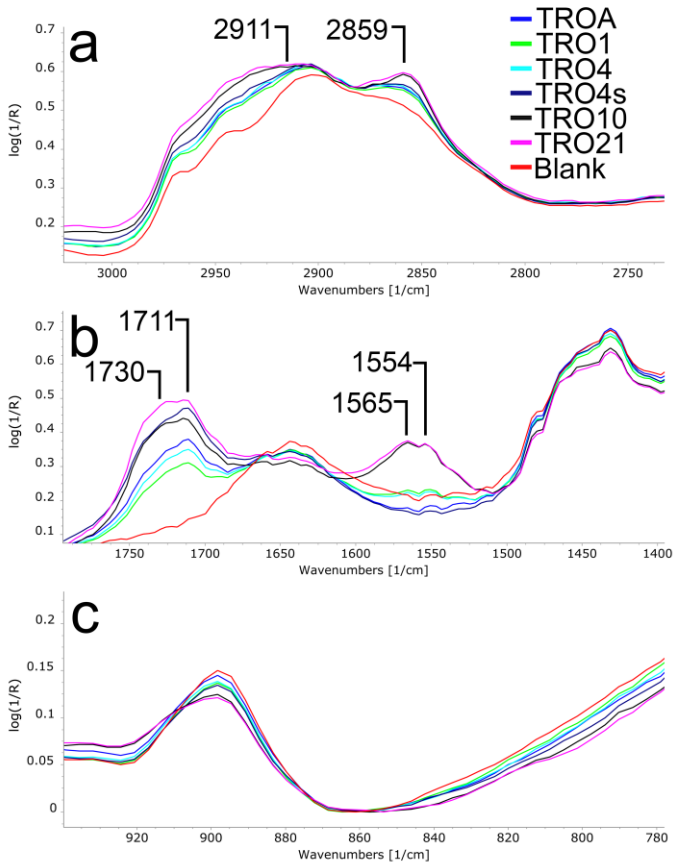


Figure 5 DRIFT spectra of calico treated with 50% aq. Turkey red oil sodium salt and heated to 60 °C for increasing time points, showing accrual of oil treatment on fibres. Peaks for TRO21.

The most pronounced spectral change from the oil treatment is the appearance of a distinct band in the carbonyl stretching region for $\nu_{asym}(C=O)$,[17] marked at 1711 cm^{-1}. Figure 5b shows it overlapping another carbonyl band around 1730 cm^{-1}. Lee *et al.* assign these to oleic acid dimers and monomers at 1712 and 1743 cm^{-1}, respectively. They note that higher concentrations of oleic acid produce more dimeric species and hydrogen bonding causes the monomeric species to shift to a lower wavenumber, in their results around 1731 cm^{-1} [25]. This is consistent with the peak

assignments at 1713 and 1732 cm^{-1} from Gong *et al.* for oleic acid dimers and monomers [24], and the spectra in Figure 5. They found that the oleic acid dimers and monomers formed hydrogen bonds with surface hydroxyl groups on the glass and mineral particles, and that additional oleate species adsorbed to the hydrogen-bonded ones via hydrocarbon chain adsorption, forming a hydrophobic layer.

Oiling treatments for Turkey red included sodium ions, either from the aq. sodium carbonate solution or the salts used to make Turkey red oil. Some spectra in Figure 5b have peaks for $\nu_{asym}(COO^-)$ at 1565 and 1554 cm^{-1}, attributed by Lee *et al.* to precipitated and coated sodium oleate, respectively [25]. Based on their inconsistent occurrence in the replica samples, they may be related to how thoroughly the samples were washed after oiling. The presence of Na^+ was found to have a significant role dissociating COOH groups and replacing them with COO−M metal salts [25]. The sodium oleate groups are ionic in nature and tend to dissociate in water [26], which explains why over-washing of the cotton after oiling risked damaging the product. The influence of the sodium ions has a more significant role in the following step, the application of aluminium, discussed later in this section. The band for ν_{str}(C-O-C) of bulk cellulose at 899 cm^{-1} in Figure 5c is indicative of asymmetric out-of-phase ring stretching for cellulose, and except for some baseline variation is consistent between samples.

4.2 Replica Turkey red

Spectra were taken from three samples each of replica Turkey red dyed with madder and with alizarin, replica Turkey red dye by a professional dyer (denoted by *), and calico dyed with madder but without oil, one from this project and the other from the professional dyer (Table 2). The replica Turkey red samples dyed for this project have peaks at 2910 and 2859 cm^{-1} for ν_{str}(−CH2−) in Figure 6a and 1713 and 1732 cm^{-1} for ν_{asym}(C=O) in Figure 6b, values consistent with the bonding described for the oiled calico samples in Figure 5. The slightly different distribution of dimers and monomers in TR* is consistent with it being prepared with rancid olive oil rather than Turkey red oil. The spectra for unoiled samples dyed with madder lack the fatty acid peaks seen in the Turkey red spectra.

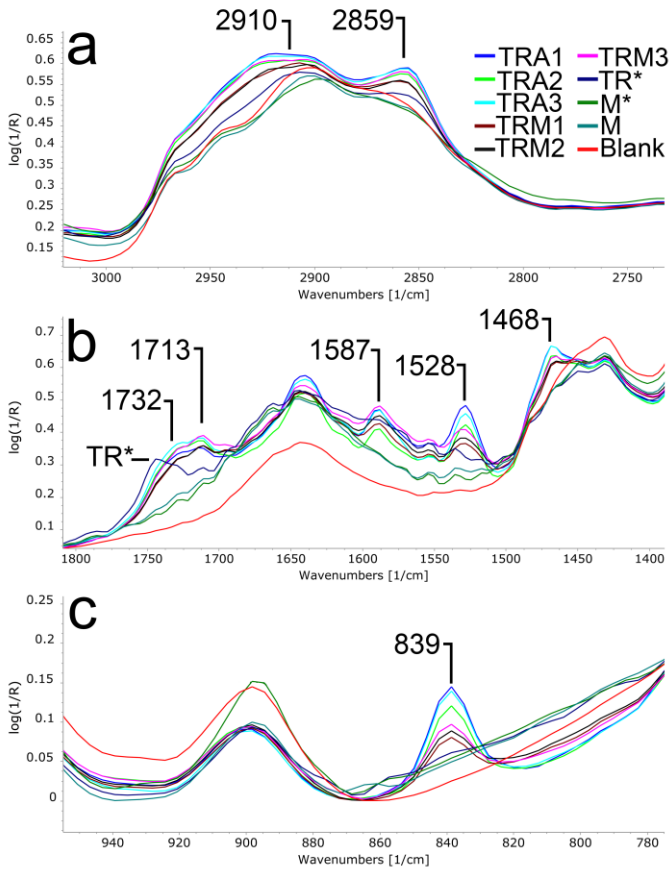


Figure 6 **Inset of DRIFT spectra for samples of replica Turkey red dyed with madder and synthetic alizarin, and calico dyed with madder and no oil. Peaks for 'TRA2'.**

The region from 1600-1400 cm^{-1} contains peaks for RCOO−M stretching. In Figure 6b, the spectra also show stretches at 1587 cm^{-1} and 1468 cm^{-1}, which are not present in the spectra of oiled calico, and are consistent with values for $\nu_{asym}(COO^-)$ and $\nu_{asym}(COO^-)$ of aluminium oleate, respectively [28]. They were also seen in an analysis of red lake pigment, attributed to the formation of aluminium soaps when the lake reacts with the oil medium [29]. Lee *et al.* found that aluminium reacted slowly with oleic acid, but readily replaced precipitated aluminium oleate by replacing Na^+ ions, and that the strongly coordinated COO-Al bond was very stable [25]. This indicates aluminium soaps are precipitated onto the fibres by the adsorbed fatty acids. The stability of these compounds and their low water solubility likely contribute to the wash fastness of Turkey red, and possibly light and rub fastness as well. The importance of washing the excess oil off the fibres prior to applying aluminium was to mitigate the formation of metal soaps in solution, where they would not contribute to the overall dyeing.

The position of these bands can be used to assign bonding geometry to the complex by Δν, calculated as $\nu_{asym}(COO^-)$ minus $\nu_{sym}(COO^-)$ [30]. This information can be used to elucidate the

structure of the Turkey red complex on the fibre. Typical bonding geometries include unidentate coordination (κ^1), bidentate chelating (κ^2), and bidentate bridging (μ^2) [27]. The value for $\Delta\nu$ in Turkey red is around 120 cm^{-1}, attributed bidentate chelation [31], bidentate bridging [28], or a combination of both [32]. Figure 7 depicts these complexes along with a fourth option, as neither bidentate complex is consistent with the Turkey red process. Papageorgiu *et al.* call the fourth complex a 'pseudo bridged' unidentate arrangement (κ^1) where one carboxylate oxygen is hydrogen-bonded while the other interacts with a metal ion [30].

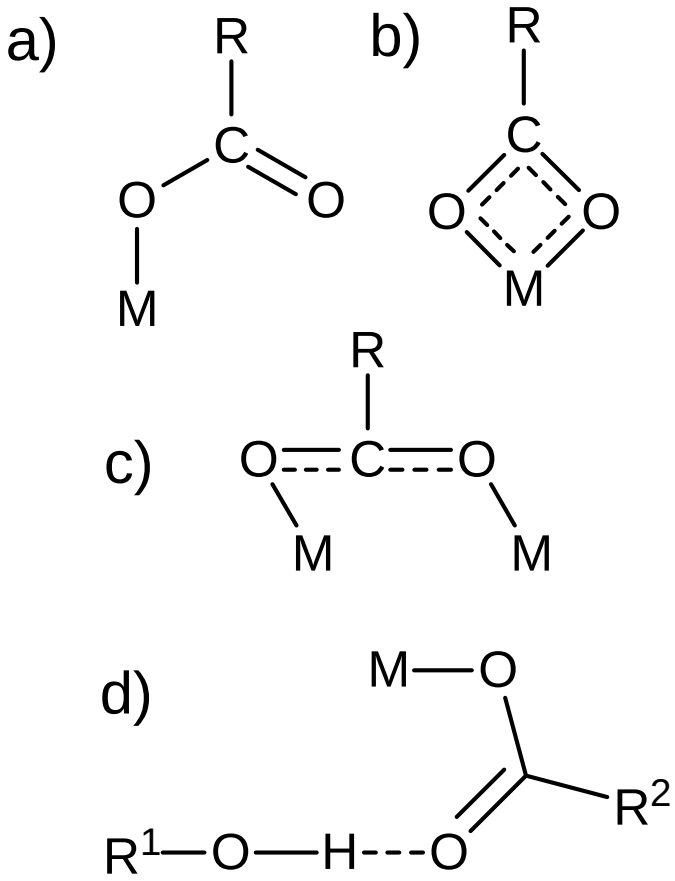


Figure 7 Metal carboxylate coordinating complexes a) unidentate coordination (κ1), b) bidentate chelation (κ2), c) bidentate bridging (μ2), and d) 'pseudo bridged' unidentate arrangement (κ1) (R1 is cellulose, R2 is fatty acid chain).

The $\Delta\nu$ calculation by Papageorgiu *et al.* for this complex is close to the values seen in this DRIFT analysis, and the geometry is applicable to the previously undescribed cellulose-fatty acid-aluminium complex of Turkey red. It also allows for the initial cellulose-fatty acid hydrogen bond, which cannot be explained through the other models. This research proposes that Turkey red is a complex built by adsorbing fatty acids onto cellulosic cotton fibres via hydrogen bonding, then precipitating aluminium soaps and forming a colour lake with hydroxyanthraquinone dyes and calcium. This

complex may also account for the increased signal around 1641 cm^{-1} in the Turkey red spectra, which corresponds to bound water. Proposed structures for the lake complex include water molecules, so this is consistent with the literature on the topic.[7,33]

In Figure 6c, the peak at 839 cm^{-1} indicates ν_{def}(C-H) out-of-plane on aromatic rings, corresponding to the uptake of anthraquinone dyes like alizarin, and not present in the blank or in Figure 5. A peak also appears in Figure 6b at 1528 cm^{-1}, consistent with the one at 839 cm^{-1} and corresponding to aromatic alkene bonds, while the region around 1679 cm^{-1} corresponds to quinones.[27] This was an unexpected result of the analysis as organic colourants are not typically abundant enough to be detected on textiles by FTIR, but in the case of Turkey red the homogeneity of the dyes structures (hydroxyanthraquinones) and their particular responsiveness to FTIR make it possible to detect the colorant in the spectra.

4.3 Historical samples

In Figure 8, the spectra for Persoz #92 and #93, which were prepared by the 'old' process based on the date of publication, are compared to those from TROA and a blank. Shoulders appear around 2910 and 2860 cm^{-1} indicative of $\nu_{asym}(-CH_2-)$ and $\nu_{sym}(-CH_2-)$, respectively, and both Persoz spectra have a peak for ν_{asym}(C=O) around 1712 cm^{-1} with a shoulder around 1731 cm^{-1}, consistent with the replica oiled calico samples. These spectra show a historical sample prepared for dyeing Turkey red by the 'old' process has similar C=O fatty acid environments to a modern replica sample prepared by the 'new' process. The changes resulting from the oil treatment are consistent with the cited studies of oleate coatings on hydroxyls and indicate the adsorption of fatty acid monomers and dimers on the cellulose hydroxyls by hydrogen bonding, with other fatty acids attaching via hydrocarbon chain adsorption.

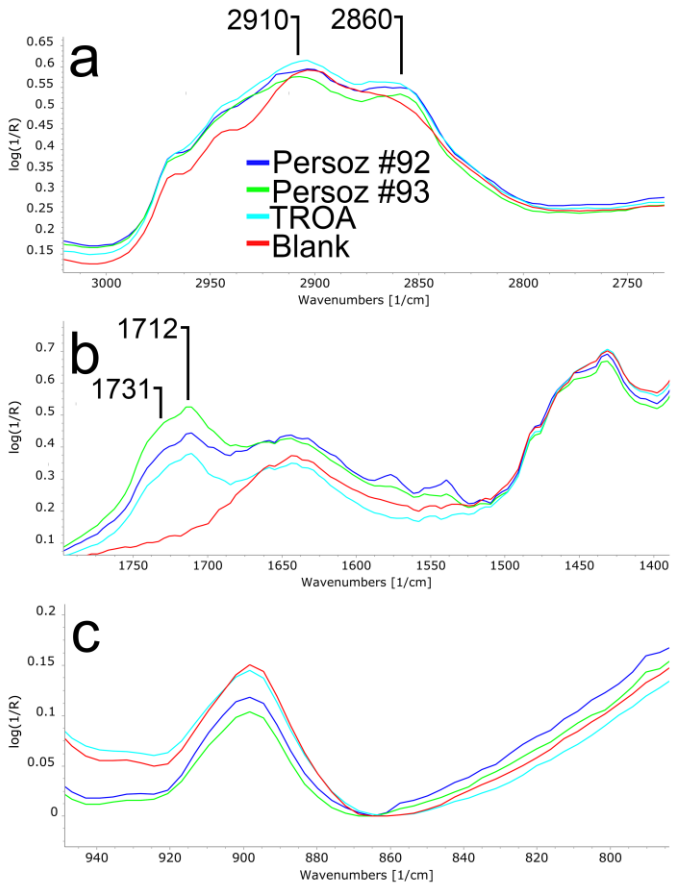


Figure 8 DRIFT spectra of mid-19th c. oiled calico prepared by the 'old' process in Persoz compared to replica oiled calico prepared with TROA. Peaks marked for Persoz #93.

Nine samples of dyed Turkey red from various stages of the process were included by Persoz, and are listed in Table 3. The spectra in Figure 9a show the same characteristics seen in previous samples, with $\nu_{asym}(-CH_2-)$ and $\nu_{sym}(-CH_2-)$ at 2909 and 2854 cm^{-1}, and $\nu_{asym}(C=O)$ around 1712 and 1731 cm^{-1} in Figure 9b. The samples also have $\nu_{asym}(COO^-)$ and $\nu_{asym}(COO^-)$ at 1587 and 1466 cm^{-1}, and anthraquinone-related bands, indicating the same aluminium complex is forming.

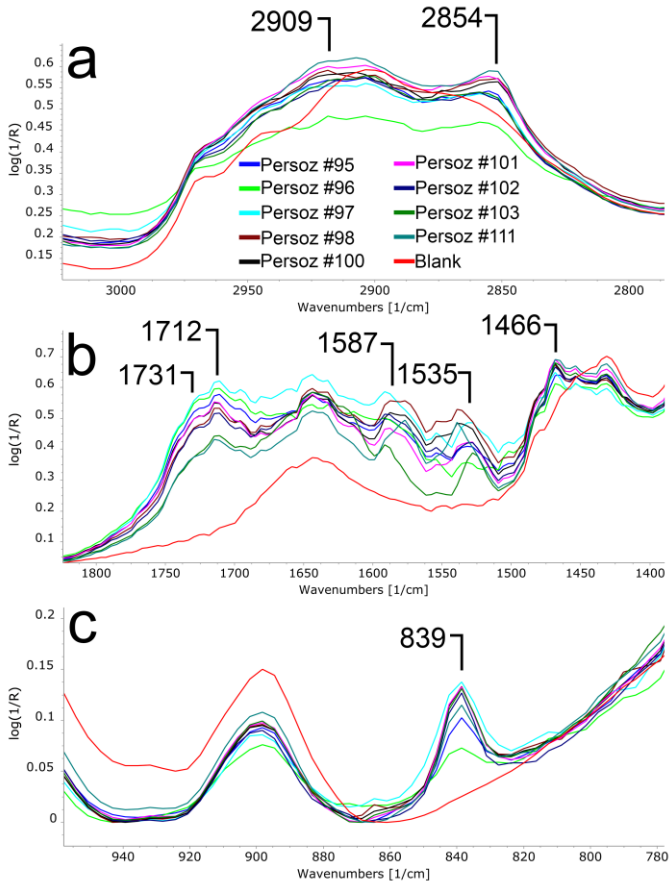


Figure 9 Inset of DRIFT spectra for samples of mid-19th c. Turkey red in Persoz. Peaks marked for Persoz #100.

The bands at 1535 and 839 cm^{-1}, as seen in the replica Turkey red samples, are again indicative of the uptake of anthraquinone dyes. This is also seen in the spectra from and six pieces of late-19th c. Turkey red from the Glasgow University archives (UTR samples), five from red areas and one from a pink area (Figure 1b). In Figure 10c, the spectrum for the pink in UGD 13/8/7 #11 is consistent with there being less hydroxyanthraquinone dye and fewer aromatic rings.[27] The spectra from the UTR samples in the rest of Figure 10 are similar to those from the replica Turkey red and the Persoz book, with the characteristic peaks for fatty acids and aluminium carboxylates present.

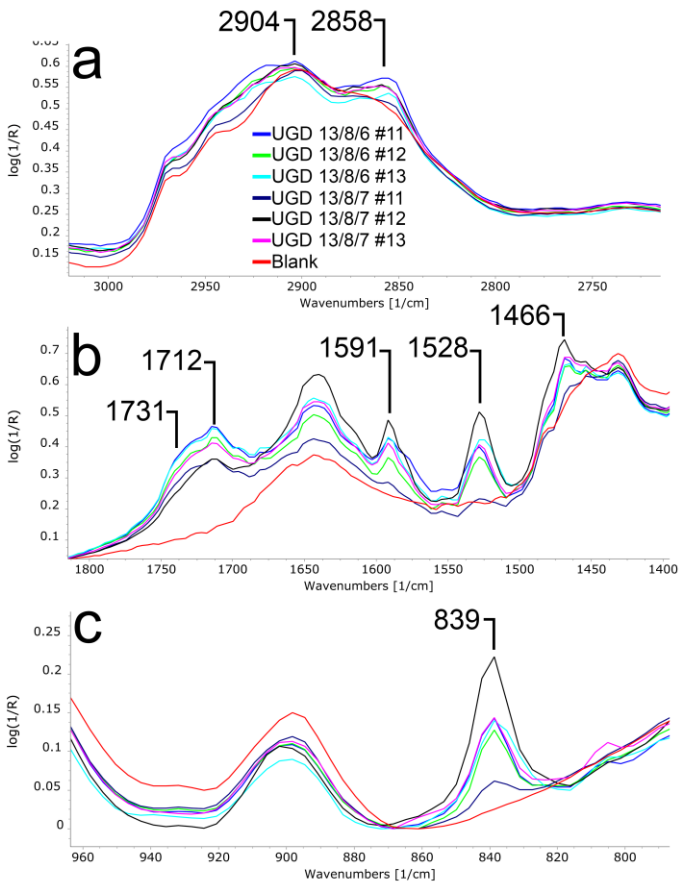


Figure 10 Inset of DRIFT spectra from late-19th c. Turkey red from the United Turkey Red Co. Ltd. Peaks marked for UGD 13/8/6 #12.

5 Conclusions

The application of DRIFT spectroscopy in heritage conservation research thus far has included built heritage [9], painting layers [10], and *in situ* pigment identification [11]. This work shows it is also a valuable tool for *in situ* analysis of the textiles mounted in fragile historical pattern books from United Turkey Red and in the pages of Persoz's dyeing manual from 1846. The results showed that on samples of replica oiled calico, fatty acids in the oil treatment form hydrogen bonds with cellulose hydroxyls as carboxylic dimers and monomers, as identified in studies by Lee *et al.* [22,23] and Gong *et al.* [24] in conditions similar to that of a Turkey red oiling process. Also, the layers of fatty acid species condense onto the fibres via hydrocarbon chain adsorption, creating a hydrophobic barrier on the fibre. The presence of sodium ions facilitates the dissociation of the COOH groups and in turn the desired formation of aluminium soaps in the subsequent aluminium salt bath of Turkey red dyeing. The DRIFT spectra show spectral absorbances for $\nu_{asym}(-CH_2-)$ and $\nu_{sym}(-CH_2-)$ at 2911 and 2859 cm^{-1}, respectively, for aliphatic chains from the oil treatment, and $\nu_{asym}(C=O)$ at 1711 cm^{-1} for fatty acid dimers and 1730 cm^{-1} for monomers. Peaks for aluminium

soaps in finished Turkey red appear at 1587 cm^{-1} for $\nu_{asym}(COO^-)$ and 1468 cm^{-1} for $\nu_{sym}(COO^-)$, values which indicate a 'pseudo bridged' unidentate association geometry as the basis for the Turkey red complex. The presence of hydroxyanthraquinone dyes was also detected via the small peak at 839 cm^{-1} for ν_{def}(C-H) out-of-plane on aromatic rings.

The dyeing manual of Persoz gives accompanying text for the Turkey red method followed for preparing the textile samples included in the book, while the UTR pieces have no such provenance. The replica Turkey red samples produced following Hummel's 19th c. method had DRIFT spectra comparable to the UTR and Persoz pieces, indicating Turkey red processes were consistent across manufacturers. Being able to finally discern the structure of Turkey red advances our understanding of these unique textiles, and through non-invasive DRIFT analysis, minimises risk to the historical objects. Understanding more about the chemistry of these pieces, and how they were so resistant to fading, can be employed to further improve conservation and display conditions for historical Turkey red, hopefully increasing collection accessibility and longevity.

6 Acknowledgements

This work was funded by the University of Glasgow Lord Kelvin Adam Smith scholarship. Thanks to Ela Gorska-Wiklow and Bob MacLean in the University of Glasgow Archives and Special Collections, Debbie Bamford for dyed samples, and Dr John Liggat in the Department of Pure and Applied Chemistry at Strathclyde University.

The authors declare that they have no conflicts of interest with this work.

7 References

[1] C.L. Berthollet, A.B. Berthollet, Éléments de l'art de la teinture, 2nd ed., Firmin Didot, Paris, 1804.

[2] J.-A.-C. Chaptal, L'art de la teinture du coton en rouge, L'imprimerie de Crapelet, Paris, 1807.

[3] R.A. Peel, Turkey Red Dyeing in Scotland Its Heyday and Decline, J. Soc. Dye. Colour. 68 (1952) 496–505. doi:10.1111/j.1478-4408.1952.tb02744.x.

[4] S. Nenadic, S. Tuckett, Colouring the Nation: The Turkey Red Printed Cotton Industry in

Scotland c.1840-1940, NMS Enterprises Limited, Edinburgh, 2013.

[5] J.H. Wertz, A. Quye, D.J. France, P.L. Tang, L. Richmond, Authenticating Turkey red textiles through material investigations by FTIR and UHPLC, in: ICOM-CC 18th Trienn. Meet. Prepr. 4-8 Sept., Copenhagen, 2017.

[6] M.R. Derrick, D. Stulik, J.M. Landry, Infrared Spectroscopy in Conservation Science, Getty Publications, Los Angelees, 2000.

[7] E.G. Kiel, Metaalcomplexen van Alizarinerood, TU Delft, 1961.

[8] E.G. Kiel, P.M. Heertjes, Metal Complexes of Alizarin V-Investigations of Alizarin-dyed Cotton Fabrics, J. Soc. Dye. Colour. 81 (1965) 98–102. papers2://publication/doi/10.1111/j.1478-4408.1965.tb02647.x.

[9] I. Arrizabalaga, O. Gomez-Laserna, J. Antonio Carrero, J. Bustamante, A. Rodriguez, G. Arana, J. Manuel Madariaga, Diffuse reflectance FTIR database for the interpretation of the spectra obtained with a handheld device on built heritage materials, Anal. Methods. 7 (2015) 1061–1070. doi:10.1039/c4ay02189d.

[10] M. Manfredi, E. Barberis, A. Rava, E. Robotti, F. Gosetti, E. Marengo, Portable diffuse reflectance infrared Fourier transform (DRIFT) technique for the non-invasive identification of canvas ground: IR spectra reference collection, Anal. Methods. 7 (2015) 2313–2322. doi:10.1039/C4AY02006E.

[11] I. Arrizabalaga, O. Gómez-Laserna, J. Aramendia, G. Arana, J.M. Madariaga, Determination of the pigments present in a wallpaper of the middle nineteenth century: The combination of mid-diffuse reflectance and far infrared spectroscopies, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 124 (2014) 308–314. doi:10.1016/j.saa.2014.01.017.

[12] T. Armaroli, T. Bécue, S. Gautier, Diffuse Reflection Infrared Spectroscopy (DRIFTS): Application to the in situ Analysis of Catalysts, Oil Gas Sci. Technol. 59 (2004) 215–237.

[13] J.J. Hummel, The dyeing of textile fabrics, 2nd ed., Cassell & Company, London, 1886.

[14] S. Steger, H. Stege, S. Bretz, O. Hahn, Capabilities and limitations of handheld Diffuse

Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for the analysis of colourants and binders in 20th-century reverse paintings on glass, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 195 (2018) 103–112. doi:10.1016/j.saa.2018.01.057.

[15] I. Arrizabalaga, O. Gómez-Laserna, J. Aramendia, G. Arana, J.M. Madariaga, Applicability of a Diffuse Reflectance Infrared Fourier Transform handheld spectrometer to perform in situ analyses on Cultural Heritage materials, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 129 (2014) 259–267. doi:10.1016/j.saa.2014.03.096.

[16] A. Sansone, Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton, J. Soc. Dye. Colour. 1 (1885) 203–211.

[17] W.H. Perkin, The History of Alizarin and Allied Colouring Matters, and Their Production from Coal Tar, J. Soc. Arts. 27 (1879) 571–608.

[18] G. Fereday, Natural Dyes, The British Museum Press, London, 2003. papers2://publication/uuid/1055C610-A01B-402B-A0FB-DF08A565BC1C.

[19] J.-F. Persoz, Traité théorique et pratique de l'impression des tissus, Victor Masson, Paris, 1846.

[20] M. Fan, D. Dai, B. Huang, Fourier Transform Infrared Spectroscopy for Natural Fibres, in: S.M. Salih (Ed.), Fourier Transform - Mater. Anal., InTech, 2012: pp. 45–68. doi:10.5772/35482.

[21] P. Garside, P. Wyeth, Identification of cellulosic fibres by FTIR spectroscopy: Thread and single fibre analysis by attenuated total reflectance, Stud. Conserv. 48 (2003) 269–275.

[22] P. Jandura, B. V. Kokta, B. Riedl, Fibrous long-chain organic acid cellulose esters and their characterization by diffuse reflectance FTIR spectroscopy, solid-state CP/MAS 13C-NMR, and X-ray diffraction, J. Appl. Polym. Sci. 78 (2000) 1354–1365. doi:10.1002/1097-4628(20001114)78:7<1354::AID-APP60>3.0.CO;2-V.

[23] C.S.R. Freire, A.J.D. Silvestre, C. Pascoal Neto, A. Gandini, P. Fardim, B. Holmbom, Surface characterization by XPS, contact angle measurements and ToF-SIMS of cellulose fibers partially esterified with fatty acids, J. Colloid Interface Sci. 301 (2006) 205–209.

doi:10.1016/j.jcis.2006.04.074.

[24] W.Q. Gong, A. Parentich, L.H. Little, L.J. Warren, Adsorption of oleate on apatite studied by diffuse reflectance infrared Fourier transform spectroscopy, Langmuir. 8 (1992) 118–124. doi:10.1021/la00037a023.

[25] D.H. Lee, R.A. Condrate Sr, FTIR spectral characterization of thin film coatings of oleic acid on glasses: I. Coatings on glasses from ethyl alcohol, J. Mater. Sci. 34 (1999) 139–146. doi:10.1023/A:1004494331895.

[26] D.H. Lee, R.A. Condrate, S.W.C. Lacourse, FTIR spectral characterization of thin film coatings of oleic acid on glasses Part II Coatings on glass from different media such as water, alcohol, benzene and air, J. Mater. Sci. 35 (2000) 4961–4970. doi:10.1023/A:1004890627405.

[27] G. Socrates, Infrared and Raman Characteristic Group Frequencies, 3rd ed., John Wiley {&} Sons, Ltd., West Sussex, 2001.

[28] W.K. Lewis, A.T. Rosenberger, J.R. Gord, C.A. Crouse, B.A. Harruff, K.A.S. Fernando, M.J. Smith, D.K. Phelps, J.E. Spowart, E.A. Guliants, C.E. Bunker, Multispectroscopic (FTIR, XPS, and TOFMS−TPD) Investigation of the Core−Shell Bonding in Sonochemically Prepared Aluminum Nanoparticles Capped with Oleic Acid, J. Phys. Chem. C. 114 (2010) 6377–6380. doi:10.1021/jp100274j.

[29] J. Kirby, M. Spring, C. Higgitt, The Technology of Eighteenth- and Nineteenth-Century Red Lake Pigments, Natl. Gall. Tech. Bull. 28 (2007).

[30] S.K. Papageorgiou, E.P. Kouvelos, E.P. Favvas, A.A. Sapalidis, G.E. Romanos, F.K. Katsaros, Metal-carboxylate interactions in metal-alginate complexes studied with FTIR spectroscopy, Carbohydr. Res. 345 (2010) 469–473. doi:10.1016/j.carres.2009.12.010.

[31] M. Mahdavi, M. Ahmad, M. Haron, F. Namvar, B. Nadi, M. Rahman, J. Amin, Synthesis, Surface Modification and Characterisation of Biocompatible Magnetic Iron Oxide Nanoparticles for Biomedical Applications, Molecules. 18 (2013) 7533–7548. doi:10.3390/molecules18077533.

[32] P. Roonasi, A. Holmgren, A Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA) study of oleate adsorbed on magnetite nano-particle surface, Appl. Surf. Sci. 255 (2009) 5891–5895. doi:http://dx.doi.org/10.1016/j.apsusc.2009.01.031.

[33] F. Delamare, B. Monasse, Computation of a Visible LIght Absorption Spectrum, a Semi-Empirical Quantum Mechanical Approach: Application to the Colour Determination of Alizarin Complexes in Solution or Chemisorbed onto Cellulose, Dye. Hist. Archaeol. 21 (2008) 214–223.